Processes and drivers of biological and chemical Phosphorus removal in wastewater treatment plants

Degree Project in Environmental Science, 15 credits

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Abstract

Phosphorus (P) is one of the most important elements exists in wastewater in soluble forms. Several methods have been using for P recovery in wastewater treatment plants, but this study tried to investigate on the most important drivers and the processes of biological phosphorus removal (EBPR) and chemical phosphorus removal that are the major technics of P recovery globally. It has been considered that EBPR is a high recovery method (normally greater than 90%) which could be implemented in different regimes with the integration feasibility of different methods, while chemical precipitation is a flexible technique that could be dosed in various section of a treatment unit. The performance and drivers of three metal-based salts such as Iron (Fe), Aluminum (Al), and Calcium (Ca) also investigated during chemical precipitation. Crystallization process is also investigated as a subcategory model of chemical P removal method. It has been considered that the alkaline pH of 9-9.5, mixing intensity, and the addition of isomorphic seed materials are the most important factors in crystallization process.

Keywords:

Enhanced biological phosphorous removal, EBPR, wastewater, chemical precipitation, crystallization, wastewater treatment plants, phosphorus recovery
# Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>II</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1. General background</td>
<td>1</td>
</tr>
<tr>
<td>1.2. Chemical phosphorus removal</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1. Crystallization</td>
<td>4</td>
</tr>
<tr>
<td>1.3. Biological phosphorus removal</td>
<td>5</td>
</tr>
<tr>
<td>2. Method</td>
<td>6</td>
</tr>
<tr>
<td>3. Discussion</td>
<td>6</td>
</tr>
<tr>
<td>3.1. Microbial assessment of EBPR</td>
<td>6</td>
</tr>
<tr>
<td>3.1.1. Anaerobic and aerobic metabolism</td>
<td>7</td>
</tr>
<tr>
<td>3.1.2. External factors</td>
<td>8</td>
</tr>
<tr>
<td>3.1.2.1. DO level</td>
<td>8</td>
</tr>
<tr>
<td>3.1.2.2. pH and temperature assessment</td>
<td>8</td>
</tr>
<tr>
<td>3.1.3. Innovative methodology</td>
<td>10</td>
</tr>
<tr>
<td>3.2. Chemical precipitation</td>
<td>11</td>
</tr>
<tr>
<td>3.2.1. Coagulants and pH assessment</td>
<td>11</td>
</tr>
<tr>
<td>3.3. Crystallization assessment</td>
<td>14</td>
</tr>
<tr>
<td>3.3.1. pH</td>
<td>14</td>
</tr>
<tr>
<td>3.3.2. Mixing intensity</td>
<td>15</td>
</tr>
<tr>
<td>3.3.3. Seed material</td>
<td>15</td>
</tr>
<tr>
<td>3.4. Advantages and disadvantages of the discussed models</td>
<td>16</td>
</tr>
<tr>
<td>4. Conclusions</td>
<td>18</td>
</tr>
<tr>
<td>5. Acknowledgment</td>
<td>VI</td>
</tr>
<tr>
<td>6. References</td>
<td>VII</td>
</tr>
</tbody>
</table>
List of Figures:

Figure 1. Phosphorus abundance in different wastewater............................................... 1

Figure 2. Feasible P recovery locations in a conventional wastewater treatment plant..... 2

Figure 3. Scheme of salt dosing locations for primary, secondary and multiple precipitations of phosphorus in the wastewater treatment process.............................. 3,4

Figure 4. The basic scheme of a conventional EBPR system with anaerobic/oxic (A/O) regime ........................................................................................................................ 5

Figure 5: the proportion of different molar ratio concentration of coagulants on P removal efficiency................................................................................................................ 12

List of Tables:

Table 1. The major added and extracted chemicals that participating in precipitation and crystallization process........................................................................................................... 4,5

Table 2. the performance of EBPR systems with A/O and A/EI regimes ....................... 9

Table 3. the various models and innovation of biological P removal in conventional condition with standard external factors ................................................................. 10,11

Table 4. The pH range of Al, Fe, and Ca salts for precipitation .................................. 13

Table 5. The advantages and disadvantages of crystallization, biological, and chemical P recovery........................................................................................................... 17
List of abbreviations

Aerobic/extended-idle (AEI)  
Aluminium (Al)  
Anaerobic/ Oxid (A/O)  
Calcium (Ca)  
Calcium phosphate (Ca-P)  
Dissolved oxygen level (DO)  
Enhanced biological phosphorus removal (EBPR)  
Forward osmosis (FO)  
Glycogen accumulating organisms (GAOs)  
Iron (Fe)  
Magnesium (Mg)  
Magnesium ammonium phosphate hexahydrate (MAP)  
Ordinary heterotrophic organisms (OHO)  
Osmotic Membrane Bioreactor (OMBR)  
Phosphorus (P),  
Phosphorus accumulating organisms (PAO)  
Polyhydroxyalkanoates (PHA)  
Polyphosphate (poly-P)  
Reverse osmosis (RO)  
Volatile fatty acids (VFAs)  
Wastewater treatment plant (WWTP)
1. Introduction
1.1. General background

Nowadays, wastewater has been considered as a rich source of energy, nutrients, and not just as a pollutant source (Mo and Zhang, 2013). Water effluent from different sources such as agricultural runoff, industrial and household sewages are consisting of notable materials which could be recovered and reused in a sustainable way (Mulkerrins et al., 2004). Among all available nutrients in wastewater, phosphorus is one of the most valuable and abundant compounds which is widely used in agriculture and chemical industry (Kube et al., 2018; Rott et al., 2017). Phosphorus is a nonrenewable source that has a mineral origin and supplying from phosphorous rocks. Due to limit access and increasing demands for P sources, the wastewater’s unused P compounds could be considered as a significant reserve alternative that could balance up the ratio of available reserves to consumption (Scholz and Wellmer, 2013). Phosphorus is more available in the aquatic phase than in soil. Besides the numerous benefits of this valuable element, the uncontrolled amount of P components in stream water could lead to negative environmental impacts e.g. eutrophication (Amann et al., 2018; Cheng et al., 2009; Mielczarek et al., 2013). Phosphorus is almost seen in all types of the wastewaters but among them, municipal sewages and livestock effluents have the most abundant that is shown in Fig.1.

![Phosphorus abundance in different wastewater sources](image)

Figure 1. Phosphorus abundance in different wastewater sources (CEEP, 2003).

Phosphorus recovery is still a very young field which could drives the unseen potential of wastewater treatment plants (WWTP) toward a profitable market. As shown in Fig.2, the recovery of phosphorus could be achieved in all three forms of water effluents which are
the liquid phase, sludge, and post-sludge phase in the shape of incinerated sludge ash (Cornel and Schaum, 2009). Nowadays, various methods and technologies have been implemented in WWTPs to acquire an optimal phosphorus recovery all around the world, but generally models and technologies are classified to three major methods that are 1) mechanical, 2) chemical, and 3) biological phosphorus removal. The most common technologies utilizing in physical phosphorus removal are filtration methods e.g. microfiltration, ultrafiltration, membrane technology, reverse osmosis (RO), forward osmosis (FO) (Peng et al., 2018a; Wang et al., 2016). Since most of the existing phosphorus in the wastewater is in the soluble form, mechanical technologies have not usually been using independently. Therefore, in most full-scale WWTPs they are considered as the co-application method that optimizing the recovery/removal of phosphorus through physio-chemical or physio-biological processes.

Figure 2. Feasible P recovery locations in a conventional wastewater treatment plant (Daneshgar et al., 2018)

1.2. Chemical phosphorus removal

The initial utilization of chemical phosphorus removal/recovery in the industrial scale was seen in the late of 1950s by chemical precipitation (Yang et al., 2006). The function of chemical precipitation is defined based on the interaction between the added chemicals (called coagulant or salt) such as Aluminum ($\text{Al}^{3+}$), Iron ($\text{Fe}^{2+}, \text{Fe}^{3+}$), or Calcium ($\text{Ca}^{2+}$) into the wastewater that tends to a strong bond with $\text{PO}_4^{3-}$ which is finally leading to P uptake (Daneshgar et al., 2018). This interaction is appearing as an insoluble salt which is mixed in sludge and needs a series of sophisticated costly processes to become reusable
In the following stage, the precipitated compounds are recovered by solid separation processes such as sedimentation, filtration, or flotation in WWTPs (Tchobanoglous et al., 2004). The precipitation process could be accomplished in various location of WWTPs as primary, secondary, and tertiary dosed. As a brief explanation, in the primary precipitation, the above-mentioned metal salts are added before the primal sedimentation stage and phosphorus is recovering from primary sludge. While, in the secondary and tertiary precipitation Al, Fe, or Ca is dosed to the activated sludge, in aeration tanks (Yeoman et al., 1988). Generally, precipitation is a flexible process that could be implemented in a solo or at multiple locations in the wastewater treatment system. Fig. 3 shows the dosing and precipitation locations of the metal salts. The chemical behavior of each one of the coagulants (Al, Fe, Ca) are unique and affected during different chemical condition. The most common chemical salts and the main extracted sediment that are contributing in P removal process are listed in Table 1.

A) Salt dosing in primary location of a wastewater plant

B) Salt dosing in secondary location of a wastewater plant
C) Salt addition on multiple locations

Figure 3. Scheme of salt dosing locations for primary, secondary and multiple precipitations of phosphorus in the wastewater treatment process (Morse et al., 1998)

1.2.1. Crystallization

Crystallization has been considered as an alternative for chemical precipitation in the 1970s (Morse et al., 1998). In this process, phosphorus is converted into the crystal powder component under metastable conditions (Chen et al., 2009). The result of the crystallization process is two chemical salts called calcium phosphate (Ca-P) and magnesium ammonium phosphate hexahydrate (MgNH₄PO₄.6H₂O-MAP) that is also known as struvite in industry. These crystallized salts are obtained in the presence of calcium and magnesium by growing on P particles as the seeding grains (Peng et al., 2018b).

<table>
<thead>
<tr>
<th>Name of methods</th>
<th>P recovery function</th>
<th>Additional chemicals</th>
<th>extracted outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Precipitation</td>
<td>Interaction between metal salts and PO₄³⁻ in the wastewater and formation of insoluble P base sediments</td>
<td>ferrous sulfate (FeSO₄), ferrous chloride (FeCl₂), FeCl₃, Fe₂(SO₄)₃, aluminum sulfate (alum), aluminum chloride (AlCl₃), aluminum chlorohydrate (Al₂Cl(OH)₃), sodium aluminate (Na₃Al₂O₄), poly-aluminum chloride (PAC), poly-aluminum sulfate, poly-aluminum chlorosulfate, slaked lime Ca(OH)₂, quick lime CaO</td>
<td>FePO₄, Fe₅(PO₄)₃, AlPO₄, 2AlPO₄, Ca₅(PO₄)₃(OH)</td>
</tr>
</tbody>
</table>
Table 1. The major added and extracted chemicals that participating in precipitation and crystallization process

| Crystallization | soluble P in the wastewater is converted to the crystal powder under metastable conditions | MgCl₂, Mg(OH)₂, magnesia (MgO), magnesite (MgCO₃), lime (CaO), CaCl₂, calcite (CaCO₃) | MgNH₄PO₄·6H₂O (struvite), Ca₃(PO₄)₂ (calcium phosphate) |

1.3. Biological phosphorus removal

Biological phosphorus removal (EBPR) is a sustainable biological wastewater treatment technology that sustainably removes phosphorus through the enrichment of activated sludge with phosphorus accumulating organisms (PAO) during a continuous cycle of anaerobic and aerobic conditions (Fig 4) (Chen et al., 2004; Vargas et al., 2009). Under anaerobic condition, PAOs consume volatile fatty acids (VFAs) as a carbon source and store them in the shape of polyhydroxyalkanoates (PHA) which is resulted in phosphorus release by hydrolysis of the stored polyphosphate (poly-P) (Oehmen et al., 2006; Vargas et al., 2009). After the transfer of activated sludge into the aerobic section, PAOs consume stored PHAs as a carbon source for energy, growth, glycogen replenishment, and phosphate uptake from poly-P during this process (Majed et al., 2009). Net of P removal occurs when the amount of up-taken P in the aerobic section is more than the amount of P release in anaerobic part (Chen et al., 2004).

Figure 4. The basic scheme of a conventional EBPR system with anaerobic/oxic (A/O) regime (Tarayre et al., 2016)
Aims

It has been tried to optimize biological and chemical P removal efficiency in recent years. To this end, a complete understanding of processes and the affecting factors on biological and chemical P removal is required. The performance of P removal systems is highly dependent on the operating condition. Several external factors impact on the efficiency of biological and chemical methods to achieve an optimal operational process. Therefore, this study strived to review the major methods that are mainly used for P recovery in the liquid phase and recognize the major factors and variable of the discussed methods. Consequently, the aim of this study is to understand what are the facilitator and inhibitory factors of biological and chemical P removal in WWTP? Furthermore, to determine the operational extent and the advantages and the disadvantages of biological and chemical P recovery methods.

2. Method

I took keywords: (Phosphorus recovery methods WWTP) on Science Direct website as the major database. I refined the keywords from 2008 to 2018 and found 1508 articles. Among them I selected 9 articles to choose my main methods. Then I divided my searches categories into 3 separated parts of biological, chemical and crystallization P recovery. In biological section 903 were found by the keywords: (EPPR processes) refined since 2000 to 2018. By adding the keyword: (carbon source) and the years: (2003-2018) I found 654 studies. I also took the keywords: (pH effect EBPR) and (microbial communication EBPR) and respectively found 579 and 35 articles. Finally, I selected 42 articles for EBPR section. In chemical P removal section, I took keywords: (phosphorous recovery wastewater chemical precipitation), refined them by the years (2003-2018) and found 1327 articles. Then I searched the keywords: (coagulant chemical precipitation phosphorus recovery) and refined the years: (2010-2018) and found 421 results. Totally 20 papers were selected for this section. For crystallization section I searched the keywords: (crystallization phosphorus recovery wastewater), refined since 2008 to 2018 and found 954 articles. I also add the keyword: (struvite) to my search from the years 2010 to 2018 and found 355 results. Finally, I selected around 19 articles for crystallization section. All in all, I selected 89 papers for all discussed methods in this study.

3.1. Microbial assessment of EBPR

Understanding of drives and processes of EBPR system requires the understanding of microbial activity during the aerobic and anaerobic phase. The existing phosphoric compounds in wastewater are essential for PAOs metabolism during the starvation
condition. As mentioned by Tarayre et al. (2016), around 9% of the general mass of microorganism’s DNA and RNA is composed by phosphorus. Although it is demonstrated that none of the microbial types is solely responsible for EBPR feasibility (Mino et al., 2001), Candidatus Accumulibacter Phosphatis has been repeatedly found as the dominant species in many laboratories scaled systems (Oehmen et al., 2005b, 2004; Pijuan et al., 2004; Zeng et al., 2003). In addition, Saunders et al. (2003) and Zilles et al. (2002) also mentioned to these bacteria as the most abundant species in real-scaled EBPR plants. For example, this study considered that the ratio of detected Candidatus Accumulibacter Phosphatis bacteria is reported 90%, 65%, 70% of all bacteria respectively in Lu et al. (2006), Oehmen et al. (2005b), and Vargas et al. (2009) studies. As well, Chen et al. (2014) devoted 32.5% of the overall biomass’s weight of their study to these bacteria. Ordinary heterotrophic organisms (OHO) and glycogen accumulating organisms (GAOs) are the group of microorganisms that competing against PAOs for carbon sources and since PAOs can uptake VFAs easier than OHO and GAOs under anaerobic condition, therefore, anaerobic phases are implementing before the aerobic sections in order to selective growth of PAOs over the other microbial communities (Vargas et al., 2009).

3.1.1. Anaerobic and aerobic metabolism

During the anaerobic phase, PAOs break VFAs and converting it to acetyl-CoA inside the cell. This digestion is required ATP consumption and the needed energy is achieved through the P transfer from poly-phosphate to ADP that in this interaction the dissolved poly-p in wastewater is converted to $\text{H}_2\text{PO}_4^-$ outside the cell (Tarayre et al., 2016). Then nicotine amide dinucleotide is the enzyme converting acetyl-CoA to PHA which is necessary for aerobic phase (Oehmen et al., 2007). Two most commonly used VFAs participating in the EBPR process are acetic and propionic acids (Chen et al., 2004). Since acetate is the largest available VFA in wastewater, it generally takes up by PAOs before other sources (Tarayre et al., 2016). therefore, adding acetate to the reactor would lead to an increase of P release. This feeding is specially applied for the conventional EBPR systems (Anaerobic/ Oxic (A/O)) that the aeration time is short and dissolved oxygen level (DO) is low (Chen et al., 2004; Yang et al., 2018). The experimental results conducted by Chen et al. (2014) showed EBPR performance is diminished in DO level of higher than 5 mg/L by supporting the available organic substrate (OHO, GAO) without contributing to P removal, however a higher P uptake could be achieved in longer time, if the reactor is fed with propionate in the same oxygen level in comparison with acetate (Zeng et al., 2013). As shown in Table 2 in recent investigations, propionate is reported as a more sustainable carbon source that could be taken up specifically by PAOs in competition with GAOs in a long-term process especially with aerobic/extended-idle (AEI) regime that the aeration time is more. Indeed, the only difference between acetate
and propionate application cycle is in aerobic phase for PHA composition where acetate is mainly stored as PHB while propionate is composed PHV and PH2MV (Vargas et al., 2009). Therefore, the presence of Competibacter in propionate fed reactor sludge is less than acetate fed reactors (Oehmen et al., 2006).

3.1.2. External factors

3.1.2.1. DO level

Apart of the design and implementation method, several external factors correspond to an optimal and sustainable performance of P recovery during EBPR process. What has been seen by this study, was the significant effect of environmental conditions on the process's efficiency. In the same way, this study believes, DO, Temperature, pH level and the type of VFA of the solution are the most important external factors that have a strong impact on EBPR efficiency. DO concentration directly affected glycogen and PHA transfiguration and also poly-P kinase activities during aerobic phase (Chen et al., 2014). There is a strong correlation between DO level and PAOs/ GAOs competition and abundance (Griffiths et al., 2002; Oehmen et al., 2007). An acceptable DO level for PAOs growth is ranged between 1-4.5 mg/L (Chen et al., 2014) however, the highest phosphorus recovery rate is reported around 3 mg/ L by different investigations (Table 2). The EBPR performance in the lowest and the highest DO level is not satisfying because the oxygen concentration of 1 mg/L and less is not easy to be sustained. On the other hand, as considered by Griffiths et al. (2002), high oxygen amount of 4.5- 5 mg/L leads to Tetrad-Forming Organisms population growth that has negative impacts on recovery process. Furthermore, the DO concentration of over 5 mg/L make GAOs stronger in the competition with PAOs (Lemaire et al., 2006). It is assumed that DO level has not remarkable effect on PH variation during EBPR process, however it might have an eligible effect in short time. For example, according to Chen et al. (2014) report, the pH level suddenly increased from 7.1 to 7.5 in the beginning of aeration period and then declined to 7.2 at the end of the aeration.

3.1.2.2 pH and temperature assessment

The higher pH is reported more beneficial for a better performance of EBPR system due to the improvement of PAOs activity during the anaerobic phase that leading to more P release (Oehmen et al., 2005a; Pijuan et al., 2004). It looks as if an EBPR system can adjust the pH around 7 automatically when the effluent pH is weak acidic or alkaline (Liu et al., 2007). A normal pH range is considered from 6.4 to 8 during the anaerobic phase that is leading to an acceptable P release (Filipe et al., 2001), but as shown in Table 2 the highest P recovery is obtaining in the pH level of 7 (Chen et al., 2014; Liu et al., 2007). Temperature is another vital factor that could affect EBPR process. The range of 10-20 C
is considering as the favorable temperature of PAOs growth that enhanced operational process (Ong et al., 2016; Panswad et al., 2003). However, a successful operation process is also reported at a lower temperature around 5°C (Brdjanovic et al., 1997). In an investigation conducted by Lopez-Vazquez (2009), it is claimed that the GAO’s activities and metabolism were inhibited due to limiting of VFAs uptake rate at 10°C. The performance of EBPR is decreasing if the temperature exceeds from 20°C. It is assumed the higher temperature of 25°C negatively affect PAOs competition against GAOs (Zheng et al., 2014). This high temperature may be considered the geographical location and seasonal variation (Barnard and Abraham, 2006; Thomas et al., 2003).

<table>
<thead>
<tr>
<th>Regime</th>
<th>DO level mg/l</th>
<th>type of VFAs</th>
<th>P removal efficiency (%)</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/EI</td>
<td>a) 0.5</td>
<td>Acetate</td>
<td>a) 98.2 ± 1.4</td>
<td>7.1-7.5</td>
<td>(Chen et al., 2014)</td>
</tr>
<tr>
<td></td>
<td>b) 3</td>
<td></td>
<td>b) 95.7 ± 1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) 5</td>
<td></td>
<td>c) 83.5 ± 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A/O</td>
<td>a) 0.5</td>
<td>Acetate</td>
<td>a) 74.5 ± 1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>b) 3</td>
<td></td>
<td>b) 90.7 ± 1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) 5</td>
<td></td>
<td>c) 78.9 ± 1.9</td>
<td>_</td>
<td></td>
</tr>
<tr>
<td>A/O</td>
<td>2 ± 0.2</td>
<td>-</td>
<td>-</td>
<td>7-8</td>
<td>(Lu et al., 2006)</td>
</tr>
<tr>
<td>A/EI</td>
<td>0.56-6.1</td>
<td>Propionate</td>
<td>95</td>
<td>8.03 ± 0.08</td>
<td>(Wang et al., 2012)</td>
</tr>
<tr>
<td>A/O</td>
<td>0.45-6.12</td>
<td>Propionate</td>
<td>83</td>
<td>8.15 ± 0.11</td>
<td>(Wang et al., 2012)</td>
</tr>
<tr>
<td>A/O</td>
<td>3.0-4.0</td>
<td>Acetate-glycerol (50:50)</td>
<td>96.2</td>
<td>7.0 ± 0.1</td>
<td>(Yang et al., 2018)</td>
</tr>
<tr>
<td>A/O</td>
<td>3.5-4.5</td>
<td>Propionate</td>
<td>-</td>
<td>7.5</td>
<td>(Vargas et al., 2009)</td>
</tr>
<tr>
<td>-</td>
<td>2</td>
<td>Propionate</td>
<td>95</td>
<td>-</td>
<td>(Coats et al., 2017)</td>
</tr>
<tr>
<td>A/EI</td>
<td>-</td>
<td>Acetate-Propionate (2.2:1)</td>
<td>94</td>
<td>7</td>
<td>(Chen et al., 2013)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>93</td>
<td>7.2-7.9</td>
<td>(Guo et al., 2018)</td>
</tr>
<tr>
<td>A/EI</td>
<td>-</td>
<td>a) Acetate b) propionate (for 50 days)</td>
<td>a) 72.4 b) 71.8</td>
<td>7.5</td>
<td>(Zeng et al., 2013)</td>
</tr>
<tr>
<td>A/EI</td>
<td>-</td>
<td>a) Acetate b) propionate (for 96 days)</td>
<td>a) 72.6 b) 92.1</td>
<td>7.5</td>
<td>(Zeng et al., 2013)</td>
</tr>
</tbody>
</table>
Table 2. The performance of EBPR systems with A/O and A/EI regimes according to different pH, DO level, and VFA type

3.1.3. Innovative methodology

Many technics have been implemented to improve the conventional (A/O) EBPR efficiency. For instance, it is suggested that P removal can be achieved without anaerobic pool if the idle time of activated sludge is increased from 210 to 450 minutes. This mechanism is called Aerobic/Extended-Idle (A/EI) regime (Chen et al., 2014, 2013; Wang et al., 2009). Another design is called EBPRr process which in that activated sludge transferred in a cycle to preparing an optimal and appropriate COD (Chemical Oxygen Demand) for phosphorus recovery (Yan et al., 2015). Valverde-Pérez et al. (2015, 2016) have implemented a biological phosphorus and recovery model which is defined as EBP2R for both microalgae cultivation and P removal. In this model orthophosphate streams diverted from the anaerobic section of EBPR system. By manipulating of the phosphate flow rate in an extra section, a controlled Nitrogen-to-Phosphorus ratio can be obtained. This conducted flow is considered as a potential source for micro-algae cultivation in downstream Photobioreactor. Another valuable model is configurated after the discovery of Denitrifying Phosphate Accumulating Organisms which allows the system assimilate Nitrogen and Phosphorus together (Wang et al., 2015). Membrane technology is another innovation that is regarded for an optimal P recovery through Osmotic Membrane Bioreactor (OMBR). There are two main methods for OMBR implementation which are defined as follow osmose and reverse osmose OMBR (Qiu and Ting, 2014). In the both OMBR-FO and OMBR-RO, phosphorus and organic compounds are removed by biological operation in the reactor, furthermore phosphate, magnesium, calcium and unconverted ammonium ions are separated and concentrated through FO and RO membrane (Luo et al., 2016; Qiu and Ting, 2014). I strived to show the P recovery performance of the discussed methods in Table 3.

<table>
<thead>
<tr>
<th>TECHNOLOGY</th>
<th>METHOD</th>
<th>FEATURE</th>
<th>P REMOVAL</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBPR</td>
<td>A/O (Anaerobic-Oxic)</td>
<td>Short aeration period, more SBR process</td>
<td>≈ 90%</td>
<td>(Chen et al., 2014)</td>
</tr>
<tr>
<td></td>
<td>A/EI</td>
<td>Resistance against high aeration time</td>
<td>≈ 95%</td>
<td>(Wang et al., 2012)</td>
</tr>
<tr>
<td>EBP2R</td>
<td>Simultaneous P and N removal, production of algae</td>
<td>72-75%</td>
<td>(Valverde-Pérez et al., 2016, 2015)</td>
<td></td>
</tr>
</tbody>
</table>
Membrane | OMBR-FO | _ | 95% | (Qiu and Ting, 2014)
| OMBR-RO | Clean water production | 95% | (Luo et al., 2016)

| EBPR | DS-EBPR | Appropriate for high sulfate and high salinity wastewater | 93% | (Guo et al., 2018)

Table 3. Various models and innovation of biological P removal in conventional condition with standard external factors

3.2. Chemical precipitation

Since the metal salt is adding before the sludge sedimentation occurrence in the primary precipitation method (Fig.3A), the system has more chance for a more proportional mixing and flocculation. This is considered as an advantage of this method due to the lower sludge mass exist in the downstream, because of the improvement of both biochemical oxygen demand and suspended solids removal during the process (Bowker and Stensel., 1990). While the advantage of secondary or simultaneous precipitation is obtained due to the direct chemical injection to activated sludge which allows this technic to use cheapest chemical salts such as ferrous sulfate (FeSO₄) and ferrous chloride (FeCl₂) in the process. Another advantage of direct chemical dosing into the secondary precipitation stage is the bio-floculation of chemical precipitates that may occur during the process. This interaction optimizes the efficiency of colloidal or fine chemical precipitates that consequently leading to lower salt dosage and increasing the quality (Yeoman et al., 1988). The advantage of simultaneous primary and secondary chemical dosage is also the deduction in chemical consumption and enhancing the operation flexibility. Although the tertiary stage technique has a high quality of effluent and been implementing in modern wastewater treatment plants, this technique needs additional facilities and more chemical that considered as the disadvantage of this technique (Morse et al., 1998).

3.2.1. Coagulants and pH assessment

It is observed that there is a big correlation between the coagulant addition and phosphorus removal from wastewater, and a higher salt dosage increases total P removal (Ge et al., 2018). The investigation conducted by Park et al. (2016) showed that, in the coagulants mol ratio concentration of 1:1, 1:2, and 1:3, the recovery efficiency was
59.2%, 81.8%, and 94.0% for alum salt, and 34.6%, 60.0%, and 82.7% for iron salt (ferric chloride), respectively. As it is shown in Fig.5 the highest P removal achieved in 1:3 mol ratio concentration of coagulants. It is also found that both ortho-Phosphate and poly-P have the same removal mechanism during coagulation process (Jenkins et al., 1971). When the molar ratio concentration of coagulants increased to 1:3 at Georgantas and Grigoropoulou (2007) investigation, a higher decreased of ortho-P proportion is observed in comparison with poly-P. The reason could be explained due to smaller ionic radius and higher negative charge per phosphorus atom in ortho-P form that makes it more suitable for coagulation process, while poly-P consists of fully oxidized phosphorus atoms that make it more stable in effluents and decrease the recovery efficiency (Georgantas and Grigoropoulou, 2007; Park et al., 2016).

![Phosphorus Removal (%)](image)

Fig.5 the proportion of different molar ratio concentration of coagulants on P removal efficiency (Park et al., 2016)

pH is considered as the most important factor that highly effect on phosphorus recovery during chemical precipitation (Banu et al., 2008). However, different coagulants have different abilities and shows unique performance at different pH levels (table 4). For example, in iron salt precipitation method, the operational pH range for ferric chloride (FeCl₃) is considered between 5-7 in Zhang et al. (2010) and 6-9 in Pham et al. (2006) investigations, however, the best performance of P removal is reported at the pH of 7 with 97% with a dosage of 140 mg l⁻¹ FeCl₃ (Gong and Zhao, 2013). In another investigation conducted by Wang et al. (2005) the high P recovery rate of 89% was achieved at the pH level of 7 under Fe₂(SO₄)₃ treatment with the molar ratio concentration of 2.95:1 that confirms the optimal pH point of iron salts dosage during chemical operation. The pH range for Aluminum salts precipitation is considered from 4 to 9 by Ge et al. (2018). However, the highest P recovery rate was from 5.7 to 5.9 for alum in Banu et al. (2008) and 6-7 for poly-aluminum chloride in Wang et al. (2005) investigations. Szabó et al.
(2008) reported a significant increase in P recovery from 80% to 98%, when the mol ratio concentration of aluminum salt raised form 1.5:1 to 2:1. The pH rate for calcium salts precipitation is ranged from 8 to 11, therefore this salt dosage is highly recommended for the wastewater with alkalinity condition (Yong-hui et al., 2006). However, the best performance of calcium precipitation is reported 8.6-9 in Dunets et al. (2015) investigation. Calcium is a cheap source for P recovery, the dewatering process of calcium sludge is simple that make it easy to handle. However, the scaling and plugging of the calcium treatment units and pipelines may cause problems during the process and considered as this salt’s disadvantage (Gong and Zhao, 2013). The most important advantage of aluminum salt utilization is the better application feasibility during acidic condition (Ge et al., 2018). Although cheap chemical cost, excellent sludge dewatering attributes, and high P removal yield are the major advantages of iron precipitation method (Wang et al., 2005), the environmental impacts such as corrosion, staining, colorful effluents, and iron transfer could be considered as the inhibitory factors (Gong and Zhao, 2013). However, despite form the advantages of iron salt precipitation method, the aluminum salt compounds have shown higher efficiency. For instance, in an experimental report conducted by Park et al. (2016), the data showed that alum had much greater recovery rate than ferric chloride in the same molar ratio concentration of coagulants. The difference in alum and ferric chloride efficiency with the same molar ratio is visible in Fig.5. It seems that the difference in the wastewater composition, the identity, stability and growth kinetic of inorganic precipitates are the reasons of difference in alum and ferric chloride efficiency for higher P removal (Jenkins et al., 1971). Even-though pH is defined as the most important factor in chemical precipitation, other variables such as: temperature, alkalinity, ionic constituents, dissolved organic matter, ionic strength, and P concentration are also considered as key factors that could be effective in chemical precipitation process (Gong and Zhao, 2013; Szabó et al., 2008).

<table>
<thead>
<tr>
<th>Salt type</th>
<th>Best pH performance</th>
<th>pH range and condition</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>7 (Neutral)</td>
<td>5-9 (Acidic - Alkaline)</td>
<td>Low cost, excellent sludge dewatering</td>
<td>Corrosion, staining, colorful runoff</td>
</tr>
<tr>
<td>AL</td>
<td>5.7-7 (Acidic - Neutral)</td>
<td>4-9 (Acidic - Alkaline)</td>
<td>High performance</td>
<td>Expensive cost</td>
</tr>
<tr>
<td>Ca</td>
<td>8.6-9 (Alkaline)</td>
<td>8-11 (Alkaline)</td>
<td>Appropriate for alkalinity condition, cheap, simple dewatering process</td>
<td>Plugging of the pipeline and precipitation unit</td>
</tr>
</tbody>
</table>

Table 4. The pH range of Al, Fe, and Ca salts for precipitation
3.3. Crystallization assessment

Several studies have strived to identify the optimizing factors of precipitation that influence crystallization process. The performance of crystallization is directly dependent on several factors such as: molar ratio of precipitating ions, pH, mixing intensity, seeding condition, and reactor type (Peng et al., 2018b). An optimal crystallization process follows a triple chemical phase: supersaturation, nucleation (crystal apparition), and crystal growth (Karapinar et al., 2006). Supersaturation is a preparatory phase that define as a motivating force for crystal production, occurring in the metastable zone (Le Corre et al., 2009). Nucleation is the crystal appearance and birth phase that has been developing in three different mechanism: 1) homogeneous crystallization, 2) heterogeneous crystallization, and 3) auto-nucleation crystallization. The former is a spontaneous process, generating in solutions with high purification. The solution in the second mechanism is consist of impure particle such as dust suspension or grain material. The third (auto-nucleation) crystallization is occurring on the surface of the existing nucleated crystals as secondary nucleation (Ferguson et al., 2014; Ohlinger et al., 1999). Among all discussed nucleation processes, heterogeneous nucleation and auto-nucleation are the most commonly used mechanism in wastewater treatment plants (Peng et al., 2018b). The time between ending of the supersaturation stage and the formation of the first crystal in the nucleation phase is called induction time that has correlation with the nucleation rate (Hanhoun et al., 2011). Since higher supersaturation is directly affected on crystal growth and cause small crystal formation, the crystallization growth phase requires a controlled nucleation process of incorporating constituent ions (Peng et al., 2018b).

3.3.1. pH

Since both C-P and MAP crystallization are a reversible process, the solution pH is the most influential parameter that could effect on the system feasibility (Wang and Nancollas, 2008). The occurrence of crystallization process is widely feasible under alkaline condition (Rahman et al., 2014), But the optimal pH condition for Ca-P is considered around 9 (Dai et al., 2018). while the optimal pH range for struvite precipitation is between 7 to 11 (Hermassi et al., 2015), which leads to HPO₄²⁻domination reaction in this range (Daneshgar et al., 2018). Also, an eye-catching increase in P recovery rate from 65.1% to 95.8% is reported by Peng et al. (2018b), when the pH level raised from 8.5 to 9.5 during Ca-P crystallization. As well, Adnan et al. (2003) stated that the increase in pH value up to 8.5 is leading to the higher P recovery efficiency up to 90%. The experimental studies have shown that the suitable pH level for Ca-P and MAP crystallization are 9.5 and 9 respectively (Dai et al., 2018; Hao et al., 2008). In contrast, higher pH level leads to composition of calcium carbonate (CaCO₃) that reduce Ca-P crystallization efficiency through the creation of ionic pairs between Ca²⁺ and CO₃²⁻.
Moreover, Matynia et al. (2006) found that the struvite crystals size decreased five times when the pH value increased from 8 to 10. Consequently, the uncontrolled increase of pH value is not only increasing the chemical treatment cost, but also reducing the P recovery yield (Sengupta and Pandit, 2011).

3.3.2. Mixing intensity

Mixing intensity can effects on crystal growth especially when the crystallization kinetic is faster than transform rate (Peng et al., 2018b). The separation and attrition in mixing state could influence the simultaneous nucleation rate which is leading to change in number of crystal size and abundance (Ye et al., 2016). In an investigation conducted by Frawley et al. (2012), the mixing intensity is reported as an effective factor on induction time. For example, the induction time was 10 minutes when the mixing rate was low on 50 rpm, while this time reduced to 1 minute when the mixing rate increase to 120 rpm. Frawley et al. (2012) reported that higher mixing rate is leading to improvement of the secondary nucleation through the increasing the surface of crystals and seeds.

3.3.3. Seed material

The crystallization process could be enhanced by adding seed materials to the system (Liu et al., 2011). The performance of seeds is defined based on increasing the crystal reaction rate and deduction the reaction time (Peng et al., 2018a). Generally, the isomorphic compounds are considered as seed material for crystallization process. The quarts sand is considered as a suitable natural seed (Battistoni et al., 2000) and struvite (MgNH₄PO₄) (Daneshgar et al., 2018), xonotlite (Ca₆[Si₆O₁₇][OH]₂) (Chen et al., 2009), calcite (CaCO₃) (Song et al., 2006), are also the most versatile isomorphic materials that using as seed during crystallization process. The crystallization efficiency by natural sands like quarts is consider lower than the isomorphic seeds with a longer induction time (Battistoni et al., 2000). As an instance, Battistoni et al. (2000) have achieved to the maximum P recovery rate of 80% during more than 100 minutes, when the system fed by quarts sand. Struvite crystals can itself utilized as the seed material in system again (Daneshgar et al., 2018). The struvite seed utilization in Yu et al. (2013) investigation led to 20.86% increase in P recovery rate of MAP crystallization method in comparison to the unseeded process. Calcite is also reported as an incredible seed material in Dai et al. (2016) investigation with the significant P recovery rate of 95.82% during the MAP crystallization. The application of xonotlite is also perfectly suitable for aqueous solution that is comparable with P rock by having 16.7% P content from the overall crystal mass (Chen et al., 2009).
3.4. Advantages and disadvantages of the discussed models

Numerous models of chemical and biological P recovery have been implemented in lab scale or in full-size. Generally, the most important advantage of the chemical precipitation is the stability of the operation during the process that makes it very reliable and suit even as a backup or polishing unite for EBPR process. Moreover, chemical precipitation is also very flexible technic and could be applied in different location of treatment plants simultaneously (Gong and Zhao, 2013). However, in contrast the expensive costs of operation, high amount of sludge production, and the strong bond between PO$_4$ and Fe or Al that makes the recovery of P from Sludge difficult are the main disadvantages of chemical P recovery (Tian et al., 2016).

Another weakness of chemical precipitations operation, is the process strong dependency to pH value, so an optimal chemical treatment is always required a continuous pH control during operation (Banu et al., 2008). The efficiency of P recovery and the cons of chemical precipitation is tried to be improved in crystallization process. However, the pros and cons of these two technologies are almost in line with each other. As a negative point, the uncontrol operation of crystallization process could leads to the spontaneous formation of struvite in unfavorable locations of treatment system e.g. in unit pipes and leads to pH increase (Daneshgar et al., 2018). Although the expensive cost of Mg$^{2+}$ and Ca$^{2+}$ ions is still considered as the preventing factor of the crystallization process in widespread use (Peng et al., 2018b), the product recovery rate and economic efficiency are much higher, and the environmental risk is too lower than chemical precipitation (Dai et al., 2017, 2016; Tarayre et al., 2016). One more advantage of crystallization is the ability of simultaneous recovery of Phosphorus and Nitrogen together, with the estimate rate of 12%P and 5%N by mass and the possibility of direct use of struvite as an agriculture fertilizer (Daneshgar et al., 2018).

Biological phosphorus removal has many advantages in comparison to the chemical precipitation model. The most important advantages of EBPR process are low sludge production, higher P recovery rate, fewer environmental impacts, and lower operation cost in comparison with the chemical P removal (Desmidt et al., 2015; Oehmen et al., 2007). Indeed, EBPR is the most economic and the best strategy of P recovery that is known in industrial scale (Wang et al., 2017). In contrast, unexpected failure of EBPR could be occurred due to mismanagement of DO level that is leading to PAO’s washing out in the system (Jin et al., 2014; Oehmen et al., 2007; Wu et al., 2014). Although EBPR is considered cheaper P recovery technology than chemical precipitation, the expenses of operational processes such as, aeration, aerobic and anaerobic transportation (sequencing batch reactor), and sludge retention time are still high and costly (Zuthi et al., 2013). EBPR is not a fast-return yield process and the efficiency of the system is improving in
long term gradually. Moreover, the geographical location of WWTPs, with the local temperature of lower 5 C and higher 30 C is considering as an inhibiting factor which reduce the EBPR efficiency (Ong et al., 2016). I decided to sum study the major advantages and disadvantages of the discussed technologies, for a better understanding, all in table 5.

<table>
<thead>
<tr>
<th>METHOD NAME</th>
<th>SUMMARY OF PROCESS</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological Phosphorus Removal</td>
<td>The soluble P content recovers during a continues anaerobic and aerobic cycle by a group of micro-organisms called PAO</td>
<td>High recovery efficiency, lower sludge production, low toxicity and environmentally friendly, affordable</td>
<td>Long recovery time, unexpected failure due to PAO’s Vulnerability over unfavorable temperature and DO and competition with GAOs</td>
</tr>
<tr>
<td>EBPR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical Precipitation</td>
<td>The process is mainly occurred by addition of metal salt (Fe, Al, Ca) and creation of P based sludge in wastewater</td>
<td>Stable operation, simple implementation, flexible operation, satisfying recovery</td>
<td>Expensive cost of chemical, high sludge production, environment pollution in case of mismanagement, difficult P extraction from sludge due to strong bond that exists between metal salts and P</td>
</tr>
<tr>
<td>crystallization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallization</td>
<td>The crystals of calcium and/or Magnesium phosphate is created on the external surface of Seed</td>
<td>High P recovery efficiency, direct use of struvite as an agricultural fertilizer, low environmental risk, simultaneous recovery of phosphorus and nitrogen</td>
<td>The expensive ion cost of Mg and Ca, operation skills are needed, limited to alkaline condition, unwanted formation of sediment in undesirable location of the system in case of mis-operation</td>
</tr>
</tbody>
</table>

Table.5. The advantages and disadvantages of crystallization, biological, and chemical P recovery
4. Conclusions

Due to the high recovery efficiency of the discussed technologies, the soluble form of phosphorus could be considered as a stable source in wastewater. Although the technical processes have been investigated during the years, some missing parts still require more investigation e.g. the microbial competition in EBPR process. External factors have also significant effect in the systems efficiency. The most important external factor in EBPR is DO level. The best performing EBPR were those adjusted with DO level of around 3 mg/l. Although it looks EBPR system can adjust pH around 7 in weak acidic and alkaline condition the chemical precipitation techniques have wider pH operational range (4-11), while the pH range for EBPR is more limited. There is a direct correlation between the molar ratio concentration of coagulants and P recovery rate. Although Alum leads to a higher recovery rate than ferric chloride in the same scale, an increase in ferric chloride dosage can improve this deficiency. Even though crystallization is a high-efficiency technique, it is only restricted to the alkaline condition. However, the optimal performance of crystallization could be achieved in an adjusted pH of 9-9.5, mixing intensity of 150 rpm, and the addition of isomorphic materials both for C-P and MAP crystallization.
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References


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My name is Javad. I studied food technology and agricultural engineering in Iran. I had an opportunity to study the master of "Applied Environmental Science". My dream came true at Halmstad University to study this major. The great Professors and wonderful facilities let me